

DISSOCIATIVE AUTOIONIZATION IN $(1 + 2)$ -PHOTON ABOVE THRESHOLD
EXCITATION OF H_2 MOLECULES

Krishna Rai Dastidar * and Ratan Kumar Das

Department of Spectroscopy

Indian Association for the Cultivation of Science

Calcutta - 700032, India

Abstract. We have theoretically studied the effect of dissociative autoionization on the photoelectron energy spectrum in $(1 + 2)$ -photon above threshold ionization (ATI) of H_2 molecules. We have considered excitation from the ground $X^1\Sigma_g^+(v = 0, j)$ state to the doubly excited autoionizing states of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetry, via the intermediate resonant $B^1\Sigma_u^+(v = 5, j)$ states. We have shown that the photoelectron energy spectrum is oscillatory in nature and shows three distinct peaks above the photoelectron energy 0.7 eV. This feature has been observed in a recent experiment by Rottke et. al., J. Phys. B **30**, 4049(1997).

* Electronic address : spkrd@iacs.ernet.in

I. Introduction

Studies on dissociative photoionization in molecular hydrogen is being pursued for several years, almost two decades, both experimentally and theoretically. In this process the molecule is excited above the dissociation threshold of the molecular ion by the single or multiphoton absorption and the doubly excited autoionizing states play a significant role to determine the photoelectron and the atomic ion spectrum. In most of the single photon experiments (Chung et al 1993, Dehmer and Dill 1978, Gardner and Samson 1975, Glass-Maujean 1986, Glass-Maujean et al 1995, He et al 1995, Ito et al 1988, 1996, Latimer et al 1992, 1993, Strathdee and Browning 1976) the molecule is excited from the ground ro-vibrational level of the ground electronic $X^1\Sigma_g^+$ state to the dissociation continuum above the ionization threshold leaving the signature of autoionization on the dissociative ionization yields. In most of the multiphoton experiments (Anderson et al 1984, Cornaggia et al 1986, Normand et al 1986, Pratt et al, 1986, 1987, Verschuur et al 1988, 1989, Xu et al 1989), the molecule is excited from the ground state to just above the ionization continuum (and below the dissociation continuum) or above the dissociation continuum, via intermediate resonant rovibrational level of $B^1\Sigma_u^+$, $E, F^1\Sigma_g^+$ or $C^1\Pi_u$ states. In the above experiments, when the molecule is excited below the dissociation threshold (i.e. when only the bound molecular ions are produced in different rovibrational levels), the role of doubly excited states on rovibrational branching of the molecular ion has been studied; also, when the molecule is excited above the dissociation threshold (i.e. when atomic ions and neutrals are produced as dissociative ionization products together with the bound molecular ions), the effect of autoionization via doubly excited states on the atomic ion spectrum and the photoelectron spectrum (PES), have been studied. Several theoretical studies (Chupka 1987, Ganguly et al 1986, Ganguly and Rai Dastidar 1988, Hazi 1974, Hickman 1987, Kanfer and Shapiro 1983, Kirby et al 1979, 1981, Rai Dastidar et al 1986) have revealed that autoionization via doubly excited autoionizing (AI) states play a dominant role in determining the autoionization lineshape and the spectrum of ionization yields i.e. photoelectrons and photoions. It has been shown that the interference of autoionization with ionization (Fano 1961), leaves its signature on (i) the autoionization lineshape, (ii) the rovibrational branching of the molecular ion in the ground state and (iii) the spectrum of the dissociative ionization products (i.e. atomic ions and photoelectrons), for the excitation

above the dissociation threshold of the molecular ion.

For the single photon excitation from the ground state, only the *ungerade* states can be accessed and the lowest of these series is situated approximately 25.5 eV above the ground state. In this case the Franck-Condon transition occurs at very low internuclear distances (around $R = 1.4a.u.$) and at very high continuum energy. But in case of resonance enhanced (m+n)-photon transition, the molecule is selectively excited to an intermediate rovibrational level of a Rydberg state and hence the Franck-Condon transition to the autoionizing state occurs at large internuclear distance. Therefore, in this REMPI (resonance enhanced multiphoton ionization) technique, the initial condition for dissociative ionization can be changed and the molecule can be excited to different continuum energies, much below the energy, reached in the single photon transition. Recently, experimental study (Rottke et al 1997) on (3+2)-photon dissociative ionization of H_2 molecules has been done by selectively exciting the $B^1\Sigma_u^+(v=5, j)$ levels, from the ground $X^1\Sigma_g^+(v=0, j)$ states by three photon absorption and then to the dissociative continuum by two-photon absorption from these intermediate resonant levels of $B^1\Sigma_u^+(v=5, j)$ state. Angle resolved photoelectron spectrum (PES) and ion spectrum have been studied and it has been found that the PES gives oscillatory structure with increase in energy.

In the present study, an attempt has been made to explain theoretically the origin of such oscillatory behaviour of PES. In this calculation we have considered (1+2)-photon dissociative ionization of H_2 molecules. The transition scheme considered here is shown schematically in Fig. 1. By the single photon transition, the molecule is first excited resonantly to the $B^1\Sigma_u^+(v=5, j)$ state from the ground $X^1\Sigma_g^+(v=0, j)$ state of the H_2 molecule and by the subsequent two-photon transition the molecule is excited from this intermediate rovibrational level of $B^1\Sigma_u^+$ state to the dissociative continuum of the molecular ion in the ground state ($X^2\Sigma_g^+$). In this transition, the doubly excited states of *ungerade* symmetry are excited and hence the dissociative autoionization process via these AI states contributes to the PES. Our aim here is to show that the dissociative autoionization process can give rise to oscillatory photoelectron spectrum, as observed in the recent experiment (Rottke et al 1997).

II. Transition Schematics

In the experiment, the H_2 molecule is first excited from the ground $X^1\Sigma_g^+(v=0)$ state to the $B^1\Sigma_u^+(v=5)$ state by three photon absorption considering three transition schemes:

$$(i)P(1) : X^1\Sigma_g^+(v=0, j=1) \rightarrow B^1\Sigma_u^+(v=5, j=0)$$

$$(ii)R(0) : X^1\Sigma_g^+(v=0, j=0) \rightarrow B^1\Sigma_u^+(v=5, j=1)$$

$$(iii)R(2) : X^1\Sigma_g^+(v=0, j=2) \rightarrow B^1\Sigma_u^+(v=5, j=3)$$

and then by two photon transition to the dissociative continuum and autoionizing states of ungerade symmetry. In our calculation we have considered (Fig. 1) single photon transition from the ground $X^1\Sigma_g^+(v=0, j=0,1,2)$ levels to the different rotational levels of $B^1\Sigma_u^+(v=5)$ state by three transition schemes mentioned above and then two photon transition from $B^1\Sigma_u^+(v=5)$ state with rotational quantum numbers $J=0,1$ and 3 to the continuum above the dissociation threshold. In this process, excitation to four autoionizing states, two lowest AI states of $^1\Sigma_u^+$ symmetry and the two lowest AI states of $^1\Pi_u$ symmetry in the Q_1 series has been considered. To get the photoelectron spectrum, the autoionization decay from these AI states to the different dissociation continua of the ground $X^2\Sigma_g^+$ state of the hydrogen molecular ion has been studied.

III. Theory

We have used the resolvent operator technique to obtain the dissociative ionization and autoionization rate. In this technique a set of equations for the matrix elements of resolvent operator $G(z) = \frac{1}{z-H}$, with respect to product states, such as $|g\rangle|n\rangle$, $|i\rangle|n-1\rangle$, $|a\rangle|n-2\rangle$, $|c_1\rangle|n-2\rangle$, $|b\rangle|n-3\rangle$ and $|c_2\rangle|n-3\rangle$. Here, $|g\rangle$ and $|i\rangle$ are the ground and the intermediate resonant states of the bare molecule, $|a\rangle$ and $|b\rangle$ are the AI states of different symmetry excited by the single photon and two photon absorption from the intermediate state of the molecule respectively and the continua $|c_1\rangle$ and $|c_2\rangle$ are excited by the single photon and two photon absorption from the intermediate state respectively (see Fig. 1). Hence the continua are of different symmetry. The continuum $|c_2\rangle$ will be of the same symmetry as the intermediate resonant state $|i\rangle$ and the continuum $|c_1\rangle$ will be of opposite symmetry. The $|n\rangle$'s are the photon number states. H is the total

hamiltonian of the molecule+photon system. z is the complex energy of the system and the imaginary part of z gives the decay rate of the system. For the $(1+2)$ -photon transitions considered here, the equations for the matrix elements of resolvent operator are given as follows:

$$(z - E_g)G_{gg} - D_{gi}G_{ig} = 1 \quad (1)$$

$$(z - E_i)G_{ig} - D_{ia}G_{ag} - \int D_{ic_1}G_{c_1g}dE_{c_1} - D_{ig}G_{gg} = 0 \quad (2)$$

$$(z - E_a)G_{ag} - \int V_{ac_1}G_{c_1g}dE_{c_1} - D_{ai}G_{ig} - \sum_b D_{ab}G_{bg} - \int D_{ac_2}G_{c_2g}dE_{c_2} = 0 \quad (3)$$

$$(z - E_b)G_{bg} - D_{ba}G_{ag} - \int D_{bc_1}G_{c_1g}dE_{c_1} - \int V_{bc_2}G_{c_2g}dE_{c_2} = 0 \quad (4)$$

$$(z - E_{c_1})G_{c_1g} - D_{c_1i}G_{ig} - V_{c_1a}G_{ag} - \sum_b D_{c_1b}G_{bg} - \int D_{c_1c_2}G_{c_2g}dE_{c_2} = 0 \quad (5)$$

$$(z - E_{c_2})G_{c_2g} - D_{c_2a}G_{ag} - \int D_{c_2c_1}G_{c_1g}dE_{c_1} - \sum_b V_{c_2b}G_{bg} = 0 \quad (6)$$

where $E_g = \epsilon_g + n\hbar\omega$, $E_i = \epsilon_i + (n-1)\hbar\omega$, $E_a = \epsilon_a + (n-2)\hbar\omega$, $E_b = \epsilon_b + (n-3)\hbar\omega$, $E_{c_1} = \epsilon_{c_1} + (n-2)\hbar\omega$ and $E_{c_2} = \epsilon_{c_2} + (n-3)\hbar\omega$ are the energies for the product states, i.e. the ground, intermediate, autoionizing states and the two continuua respectively. Here ϵ 's are the energies for the bare molecular states. D_{jk} 's are the dipole transition moments between the product states j and k . The summation over b indicates that contribution from all the autoionizing states excited by this transition schemes has been considered. Formally obtaining G_{c_1g} and G_{c_2g} from equations (5) and (6) and substituting in equations (2),(3) and (4) one can derive equations as follows:

$$Z_gG_{gg} - D_{gi}G_{ig} = 1 \quad (7)$$

$$Z_iG_{ig} - D_{ig}G_{gg} - B_{ia}G_{ag} - \sum_b C_{ib}G_{bg} = 0 \quad (8)$$

$$Z_aG_{ag} - B_{ai}G_{ig} - \sum_b K_{ab}G_{bg} = 0 \quad (9)$$

$$Z_bG_{bg} - K_{ba}G_{ag} - C_{bi}G_{ig} = 0 \quad (10)$$

where,

$$Z_g = z - E_g$$

$$Z_i = z - E_i - s_i + \frac{i}{2}\gamma_i$$

$$Z_a = z - E_a - S_a + \frac{i}{2}\Gamma_a - s_a + \frac{i}{2}\gamma_a + 2R_{ac_1c_2a}$$

$$Z_b = z - E_b - S_b + \frac{i}{2}\Gamma_b - s_b + \frac{i}{2}\gamma_b + 2R_{bc_2c_1b}$$

$$B_{ia} = Q_{ia} - R_{ic_1c_2a}$$

$$C_{ib} = Q_{ib} - R_{ic_1c_2b}$$

$$K_{ab} = Q_{ab} - R_{ac_1c_2b} - R_{ac_2c_1b}$$

$$Q_{ia} = D_{ia} + \frac{1}{A} \int \frac{D_{ic_1}V_{c_1a}}{z - E_{c_1}} dE_{c_1}$$

$$Q_{ib} = \frac{1}{A} \int \frac{D_{ic_1}D_{c_1b}}{z - E_{c_1}} dE_{c_1}$$

$$Q_{ab} = D_{ab} + \frac{1}{A} \int \frac{D_{bc_1}V_{c_1a}}{z - E_{c_1}} dE_{c_1} + \frac{1}{A} \int \frac{D_{ac_2}V_{c_2b}}{z - E_{c_2}} dE_{c_2}$$

and

$$R_{jc_pc_qk} = \frac{\pi^2}{A} |Y_{jc_p} D_{c_pc_q} X_{c_qk}|$$

j,k corresponds to bound product states; $c_{p,q}$ corresponds to product states for continua; X_{c_qk} and Y_{jc_p} correspond to coupling terms between the continuum $c_{p,q}$ and the bound states designated by k and j respectively. Here $A = \frac{1}{1+\pi^2|D_{c_1c_2}|^2}$; γ_j and s_j are the photoionization width and ac-Stark shift, divided by the factor A, of the bound states designated by j respectively; $\Gamma_{a,b}$ and $S_{a,b}$ are the autoionization width and the shift, divided by the factor A, of the autoionizing states designated by a and b respectively, due to the configuration interaction couplings V_{ac_1} and V_{bc_2} with the continuum adjacent to the AI states. The terms involving integration over continuum (as in Q_{ia} , Q_{ib} , Q_{ab} etc.) can be expressed as the sum of the principal value part and the imaginary part in the usual manner. In the present work we have neglected the principal value part and used the pole approximation to derive the final formula for autoionization rate. Equations (8) \rightarrow (10) can be rewritten in terms of the detunings (δ_i , δ_a and δ_b) from the intermediate and two AI states respectively by substituting $z = Z_g + E_g$ in the above equations. By solving above equations one can formally obtain the matrix elements for the resolvent operator and by inverse Laplace transformation of these matrix elements one can get corresponding matrix elements for the evolution operator. Hence the probability for ionization can be written as: $P(t) = 1 - |U_{gg}(t)|^2 - |U_{ig}(t)|^2 - |U_{ag}(t)|^2 - |U_{bg}(t)|^2$.

In the weak field limit i.e. considering dipole transition strength from the ground state to the intermediate state to be much weaker than that for the ionizing transitions and the autoionizing decay, one can write down $G_{gg} = \frac{1}{Z_g - Z_0}$, where

$$Z_0 = \frac{|D_{ig}|^2}{Z_i - \sum_b \frac{C_{bi}^2}{Z_b} - \frac{[B_{ia} + \sum_b \frac{K_{ab} C_{bi}}{Z_b}]^2}{Z_a - \sum_b \frac{K_{ab}^2}{Z_b}}}$$

and hence the rate for ionization $\frac{dP}{dt} = -2ImZ_0$.

By neglecting the higher order contributions, it can be shown that the rate for dissociative autoionization via the AI states $|b\rangle$ can be written as:

$$\frac{dP_2}{dt} = \frac{4\pi^3 |D_{gi}|^2 |D_{ic_1}|^2 |D_{c_1b}|^2 |V_{bc_2}|^2}{CA^3 |Z_b|^2} \quad (11)$$

where $C = |Z_i - \sum_b \frac{C_{bi}^2}{Z_b}|^2$; $\frac{dP_2}{dt}$ can also be expressed as

$$\frac{dP_2}{dt} = \mathcal{M}_{gc_2} F \quad (12)$$

where, $F = \frac{4\pi^3}{CA^3 |Z_b|^2}$, is the lineshape factor and the modified dissociative autoionization matrix element square $\mathcal{M}_{gc_2} = |D_{gi}|^2 |D_{ic_1}|^2 |D_{c_1b}|^2 |V_{bc_2}|^2$

IV. Calculations

In the present study we have considered contribution from the dissociative autoionization via two lowest AI states of $^1\Sigma_u^+$ symmetry and two lowest AI states of $^1\Pi_u$ symmetry. The energies and autoionization widths for these four states are available in the literature Guberman 1983, Kirby et al 1981, Tennyson 1996). As mentioned before, we have considered here (1+2)-photon transition from the ground state to the autoionizing states via the intermediate resonant $B^1\Sigma_u^+$ state. Therefore, to calculate the two-photon term via the continuum, one needs to have the electronic wavefunctions for the AI states. The wavefunctions for two lowest AI states of $^1\Sigma_u^+$ symmetry have been obtained by minimizing the energy variationally. The molecular basis set used is a multi-configuration minimal basis constructed with linear combination of Slater-type atomic orbitals. We have used seven configuration wavefunctions constructed with atomic orbitals of s and p symmetry and the principal quantum number upto 4. At each value of R (internuclear separation),

all the exponents have been varied to obtain minimum energy. The energies obtained are in good agreement with the previous values (Guberman 1983) except at lower values of internuclear separation $R \leq 1.4a.u.$. Calculated energies for the second $^1\Sigma_u^+$ AI state differ by $\leq .006$ a.u. from the previous values (Guberman 1983), except at $R = 1.0$ a.u., where the difference is .017 a.u.. For the first $^1\Sigma_u^+$ AI state, the difference in energies (our results and Guberman's results) are $\leq .0086$ a.u., except at $R = 1.0$ and $R = 1.4$ a.u., where the differences are .023 a.u. and .012 a.u. respectively. The electronic wavefunctions for the ground and the intermediate states have been obtained from our previous calculations (Khatun and Rai Dastidar 1995). For the calculation of the complex nuclear wavefunctions using complex potential for the AI states, we have used modified Numerov method (Lane and Geltman 1967, Rai Dastidar and Rai Dastidar 1979).

To calculate two-photon dipole transition moment between $B^1\Sigma_u^+$ state and the AI states (i.e. to evaluate Q_{ib} ; see section III) we have used the pole approximation to integrate over the continuum energy (E_{c_1}), and hence considered contributions from the continua associated with the bound vibrational levels of the $X^2\Sigma_g^+$ state of H_2^+ ion, which are energetically below the continuum energy excited by the first photon from the $B^1\Sigma_u^+$ state. We have used the multipolar gauge to evaluate dipole transition moments, but one can also use the minimal coupling gauge. Since, in the present work, the two-photon term acts as a constant (with respect to PE energy) multiplying factor to the autoionization amplitude-square (see equation 12), the structure of the PES is independent of the choice of gauge. However, the scaling factor for PES can be different, depending on the magnitude of two-photon term in two different gauges. For the present study we have calculated the two-photon dipole transition moments for the transition from the $B^1\Sigma_u^+$ state to the two lowest AI states of $^1\Sigma_u^+$ symmetry only. It is found that the second AI state of $^1\Sigma_u^+$ symmetry is energetically very close to the lowest AI state of $^1\Pi_u$ symmetry (Guberman 1983, Tennyson 1996)) and the difference between the values of effective principal quantum numbers for these two states are also very small (Tennyson 1996). Therefore for the present calculation we have used the same two-photon dipole transition term for the transition to the lowest AI state of $^1\Pi_u$ symmetry as that calculated for the transition to the second AI state of $^1\Sigma_u^+$ symmetry. For the second $^1\Pi_u$ state we have used the same two-photon term and it is found that the contribution from this second $^1\Pi_u$ state is much smaller than that from the second $^1\Sigma_u^+$ state and the lowest $^1\Pi_u$ state.

The electronic configuration interaction term between AI state and the continuum has been derived as $V_{bc_2}(R) = \sqrt{\frac{\Gamma_b(R)}{2\pi}}$, where autoionization widths $\Gamma_b(R)$ have been obtained from the literature (Tennyson 1996) and this value of V_{bc_2} has been considered to be arising from $l = 1$ partial wave only. This is a valid approximation, since $l = 1$ is the most dominant contribution for autoionization from $^1\Sigma_u^+$ AI states (Kirby et al 1981). To obtain autoionization amplitude, integration over nuclear coordinates have been done considering explicit dependence of the electronic transition amplitudes on the internuclear separation. Similarly, to obtain dipole transition amplitudes, explicit dependence of electronic dipole transition moments on the internuclear separation (for bound-bound transition) and also on the photoelectron energy (for bound-continuum transition) has been considered for nuclear integration.

The autoionizing states lying above the dissociation continuum of the molecular ion can decay into the dissociation continua lying between the final continuum energy excited by two-photon transition from the $B^1\Sigma_u^+$ state and the dissociation threshold of the ground state ($X^2\Sigma_g^+$) of the molecular ion. Hence the total energy E_t , can be expressed as $E_t = E_e + D_e$, where E_e is the photoelectron energy and D_e is the energy of the dissociation continuum of the molecular ion. We have calculated the dissociative autoionization matrix element for the transitions to a range of dissociation continuum of the ground state of the H_2^+ ion, chosen (arbitrarily) to lie on a grid of .01 eV spacing.

V. Results and Discussions

A schematic diagram for the transitions considered here is shown in fig.1. For different molecular potential energy curves we refer to Fig.1 of Rottke et al, 1997. The two continua shown in Fig. 1 are of different symmetry and correspond to the first ionization threshold ($H_2^+(X^2\Sigma_g^+) + e$) of the neutral molecule. Results for three different transition schemes ($P(1)$, $R(0)$ and $R(2)$), i.e. for ionizing transitions from $J = 0$, $J = 1$ and $J = 3$ of $B^1\Sigma_u^+(v = 5)$ state are shown in Figs. 2,3 and 4 respectively. In these figures we have plotted the dissociative autoionization rate divided by I^3F (where I is the laser intensity and F is the line shape factor, see equ. 12), as a function of photoelectron energy. The factor I^3F , which is independent of the photoelectron energy, merely plays the role of a scaling factor as far as the shape and the structure of the

PES is concerned. The experimental PES is given in arbitrary units and here we compare our theoretical PES (scaled by the factor I^3F) with experiment. It is to be mentioned here that, for photoelectron energies less than 0.7 eV, the contribution from the ionization of neutral atoms is dominating (Rottke et al 1997) and hence the effect of dissociative autoionization will be prominent only for energies ≥ 0.7 eV. Therefore, we will discuss the features obtained in PES for energies above 0.7 eV (experimental results also show PES above 0.7 eV, see fig.2 of Rottke et al, 1997).

For this calculation we have taken $A = 1$, since the value of $|D_{c_1c_2}|^2$ is much less than unity for this calculation. The continuum-continuum transition amplitude ($|D_{c_1c_2}|$) will be significant only for photoelectron energies very close to each other (Gordon 1929) and for the present study the photoelectron energies for the transition to the lower continuum (due to the absorption of single photon from the $B^1\Sigma_u^+(v = 5)$ state) are less than .02 a.u. (i.e. less than 0.54 eV). Hence the value of $|D_{c_1c_2}|^2$ will be significant for photoelectron energies less than 0.54 eV for continuum-continuum transition. To get an estimate, we have calculated electronic dipole transition moment for continuum-continuum transition (Gordon 1929) and the overlap between the three lowest vibrational levels of molecular ion in the ground state, with different dissociation continuum of the same. It is found that the contribution from this term is orders of magnitude smaller than unity (Rai Dastidar 1996).

In the figures (2, 3 and 4), individual contributions to dissociative autoionization from four (first two $^1\Sigma_u^+$ and first two $^1\Pi_u$) autoionizing states have been shown, together with their sum. It is found that the PES is oscillatory in nature and the dissociative autoionization from the second AI state of $^1\Sigma_u^+$ symmetry is the most important contribution. We have checked that the oscillation is essentially the same as in the Franck-Condon overlap (mod-squared) between the complex nuclear wavefunction of the autoionizing state and the nuclear continuum of the molecular ion in the ground state, as a function of photoelectron energy. The PES for autoionization from three AI (second $^1\Sigma_u^+$ and the two $^1\Pi_u$) states show three peaks above the photoelectron energy greater than 0.7 eV and the peak positions are almost the same for these three PES. But the contribution from the lowest $^1\Sigma_u^+$ state is much smaller than that from the second $^1\Sigma_u^+$ state and shows an out of phase oscillation. The presence of three peaks in PES, above 0.7 eV of photoelectron energy, has also been experimentally observed (Rottke et al 1997). From the figure for PES (Fig. 2 of Rottke et

al 1997), the peak positions can be approximately calculated and we find that the peaks are shifted towards higher energy than that obtained in the present calculation. These shifts are different for three transition schemes and the values are approximately within $0.23 - 0.24$ eV, $0.17 - 0.2$ eV and $0.04 - 0.09$ eV for the first, second and the third peak respectively. It is to be mentioned here that the shifts of the autoionizing states due to autoionization decay have not been considered in our calculation. By using the approximate formula (Ganguly and Rai Dastidar 1988, Olsen 1982) $S_b = -\frac{3}{2\pi}\Gamma_b$, one can calculate the approximate values of shift (S_b) for the second AI state of $^1\Sigma_u^+$ symmetry (using the values of width tabulated by Tennyson, 1996). Typical values of shift varies from -0.02 to -0.16 eV, in the range of internuclear separation, $R = 3.0$ to 4.0 and since this value is subtracted from the energy of the AI state, electronic potential energies will be shifted upwards. Hence the peak positions in figs. 2, 3 and 4 will be shifted towards higher energy and this shifting will be different for different photoelectron energies. The values of shifts are 0.2, 0.16 and 0.14 eV for the first, second and the third peak respectively. It is found that, after shifting, the peak positions are almost the same as those observed in the experiment. It is within .03 to .04 eV, .01 to .04 eV and .05 to 0.1 eV for the first, second and the third peak respectively. But for comparing our results with the experimental PES, the resolution factor for the experiment has to be taken into account (in particular for determining the peak positions). It has been mentioned by Rottke et al, 1997 that the resolution is .08 eV at 2 eV photoelectron energy but that for energies lower than 2 eV has not been mentioned. We expect that the resolution will be better as the photoelectron energy is decreased and we find that the agreement is better for the first two peak positions than the third one.

By comparing figures 2, 3 and 4, it is found that the PES for three transition schemes are of the same order of magnitude and the PES for transition from $J = 1$ level (Fig. 3) is greater in magnitude than that from $J = 0$ (Fig. 2) and $J = 3$ (Fig. 4) levels of $B^1\Sigma_u^+(v = 5)$ state. However, in the experiment, although the contribution for these three transition schemes are of the same order (in arbitrary unit), photoelectron yield for transition from $J=0$ level of $B^1\Sigma_u^+(v = 5)$ state is greater than that from other two transitions. By analyzing our results, we find that the (1+2)-photon term for transition to the second $^1\Sigma_u^+$ AI state is greater for excitation from $j = 0$ level of the ground $X^1\Sigma_g^+(v = 0)$ state than that from other j levels. In the present work, we have done ab-initio calculations to obtain the PES for dissociative autoionization from

two $^1\Sigma_u^+$ AI states. But to obtain PES from two $^1\Pi_u$ AI states we have used the same (1+2)-photon term as calculated for second $^1\Sigma_u^+$ state. Hence the scaling factor for contribution from these two AI states ($^1\Pi_u$) may become different for three transition schemes, if the actual values of (1+2)-photon term for excitation to these two $^1\Pi_u$ states are obtained. Moreover, the values of (1+2)-photon term may differ in two different gauges (minimal coupling and multipolar). Therefore, at this stage, this difference between our results and the experiment may arise, as far as the relative magnitudes of three PES (for transitions from $J = 0, 1,$ and 3) are concerned. Nevertheless, further study in this field is warranted.

In conclusion, we have shown that the oscillatory nature of the experimentally observed PES in (3+2)-photon above threshold ionization of H_2 molecules, can be accounted for by considering the dissociative autoionization of the doubly excited autoionizing states (of *ungerade* symmetry) above the dissociative ionization threshold.

Acknowledgement

This work has been sponsored by DST, Govt. of India, Project No. *SP/S2/L* – 09/94. RKD is grateful to DST, Govt. of India for awarding Junior Research Fellowship. We are thankful to Prof. A. Suzor-Weiner for helpful discussions and drawing our attention to the paper by Tennyson, 1996. We are also thankful to Prof. T.K. Rai Dastidar for critically reading the manuscript.

References

- Anderson L, Kubiak G D, and Zare R N 1984 *Chem. Phys. Lett.* **105** 22
- Chung Y M, Lee E M, Masuoka T and Samson J A R, 1993 *J. Chem. Phys.* **99** 885
- Chupka W A 1987 *J. Chem. Phys.* **87** 1488
- Cornaggia C, Normand D, Morellec J, Mainfray G and Manus C 1986 *Phys. Rev. A* **34** 207
- Dehmer J L, and Dill D 1978 *Phys. Rev. A* **18** 164
- Fano U 1961 *Phys. Rev.* **124** 1866
- Ganguly S, Rai Dastidar K and Rai Dastidar T K 1986 *Phys. Rev. A* **33** 337

- Ganguly S and Rai Dastidar K 1988 *Phys. Rev. A* **37** 1363
- Gardner J L and Samson J A R 1975 *Phys. Rev. A* **12** 1404
- Glass-Maujean M 1986 *J. Chem. Phys.* **85** 4830
- Glass-Maujean M, Frohlich H and Martin P 1995 *Phys. Rev. A* **52** 4622
- Gordon W 1929 *Anns. of Phys.* **5** 1031
- Guberman S L 1983 *J. Chem. Phys.* **78** 1404
- Hazi A U 1974 *J. Chem. Phys.* **60** 4358
- He Z X, Cutler J N, Southworth S H, Hughey L R and Samson J A R 1995 *J. Chem. Phys.* **103** 3912
- Hickman A P 1987 *Phys. Rev. Lett.* **59** 1553
- Ito K, Hall R I, and Ukai M 1996 *J. Chem. Phys.* **104** 8449
- Ito K, Lablanquie P, Guyon P-M and Nenner I 1988 *Chem. Phys. Lett.* **151** 121
- Kanfer S and Shapiro M 1983 *J Phys. B: At. Mol. Phys.* **16** L655
- Khatun J and Rai Dastidar K 1995 *Phys. Rev. A* **52** 2971
- Kirby K, Guberman S and Dalgarno A 1979 *J. Chem. Phys.* **70** 4635
- Kirby K, Uzer T, Allison A C and Dalgarno A 1981 *J. Chem. Phys.* **75** 2820
- Lane N F and Geltman S 1967 *Phys. Rev.* **160** 53
- Latimer C J, Dunn K F, Kouchi N, McDonald M A, Srigengan V and Geddes J 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** L595
- Latimer C J, Irvine A D, McDonald M A and Savage O G 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** L211
- Olsen T 1982 Ph.D. Dissertation, University of Southern California
- Normand D, Cornaggia C and Morellec J 1986 *J. Phys. B: At. Mol. Phys.* **19** 2881
- Pratt S T, Dehmer P M and Dehmer J L 1986 *J. Chem. Phys.* **85** 3379
- 1987 *J. Chem. Phys.* **86** 1727
- Rai Dastidar K, Ganguly S and Rai Dastidar T K 1986 *Phys. Rev. A* **33** 2106
- Rai Dastidar K 1996 *Phys. Rev. A* **53** 2881 Rai Dastidar K and Rai Dastidar T K 1979 *J. Phys. Soc. of Japan* **46** 1288
- Rottke H, Ludwig J and Sandner W 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 4049

Strathdee S and Browning R 1976 *J. Phys. B: At. Mol. Phys.* **9** L505

—1979 *J. Phys. B: At. Mol. Phys.* **12** 1789

Tennyson J 1996 *Atomic Data and Nuclear Data Tables* **64** 253

Verschuur J W J, Noordan L D, Bonnie J H M and van Linden van den Heuvell H B 1988 *Chem. Phys. Lett.* **146** 283

Verschuur J W J and van Linden van den Heuvell H B 1989 *Chem. Phys.* **129** 1

Xu E, Hickman A P, Kachru R, Tsuboi T and H Helm 1989 *Phys. Rev. A* **40** 7031

Xu E Y, Tsuboi T, Kachru R and Helm H 1987 *Phys. Rev. A* **36** 5645

Figure Captions

fig. 1: Schematic diagram for $(1 + 2)$ -photon above threshold ionization. Two continua $|c_1\rangle$ and $|c_2\rangle$ are of *gerade* and *ungerade* symmetry respectively and correspond to the first ionization threshold $(H_2^+(X^2\Sigma_g^+) + e)$ of the hydrogen molecule.

fig. 2: Dissociative autoionization rate divided by I^3F (see text, equ. 12), where I is the laser intensity and F is the lineshape factor, has been plotted as a function of photoelectron energy, for two-photon ionizing transition from rotational level, $J=0$ of $B^1\Sigma_u^+(v=5)$ state. Contributions from four AI states and their sum have been shown separately. Legends for the curves are: - - - contribution from the lowest $^1\Sigma_u^+$ AI state; **** same from second $^1\Sigma_u^+$ AI state; ++++ same from lowest $^1\Pi_u$ AI state; $\diamond\diamond\diamond$ same from the second $^1\Pi_u$ state and - sum total of the four contributions.

fig. 3: Same as in Fig. 2, for transition from $J=1$ level of $B^1\Sigma_u^+(v=5)$ state.

fig. 4: Same as in Fig. 2, for transition from $J=3$ level of $B^1\Sigma_u^+(v=5)$ state.

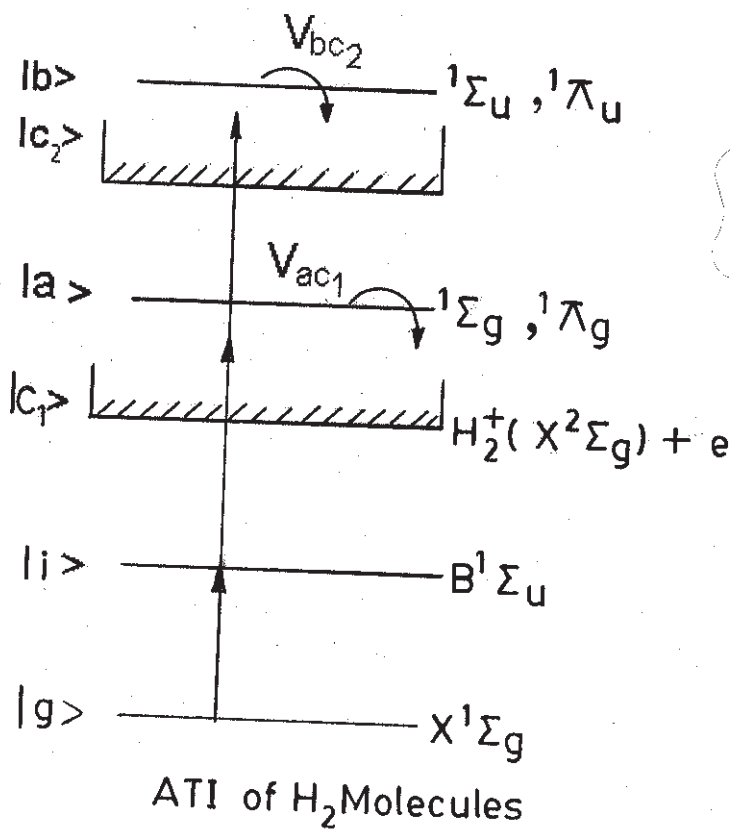


Fig. 1

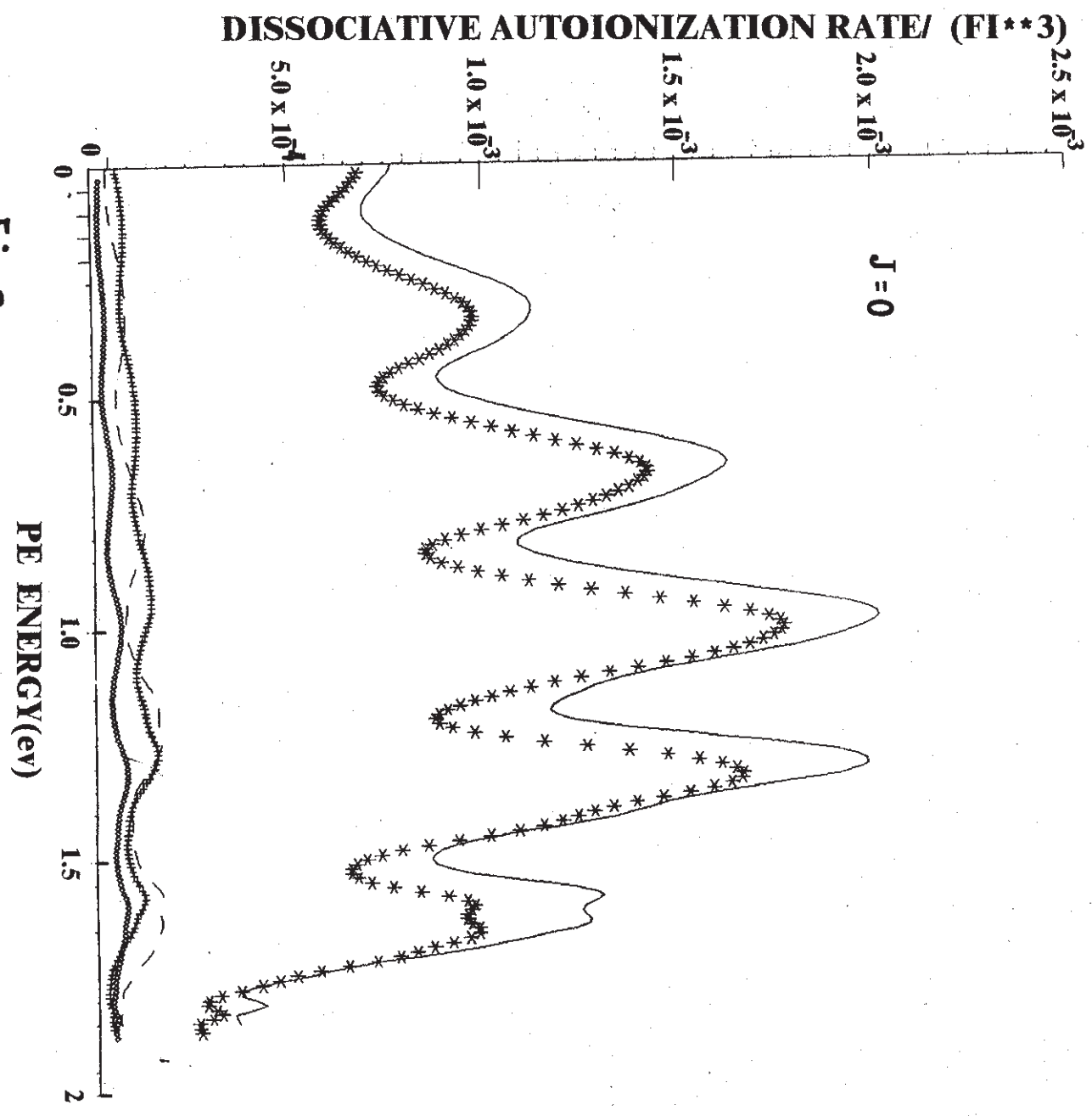


Fig.2

DISSOCIATIVE AUTOIONIZATION RATE / (FI** 3)

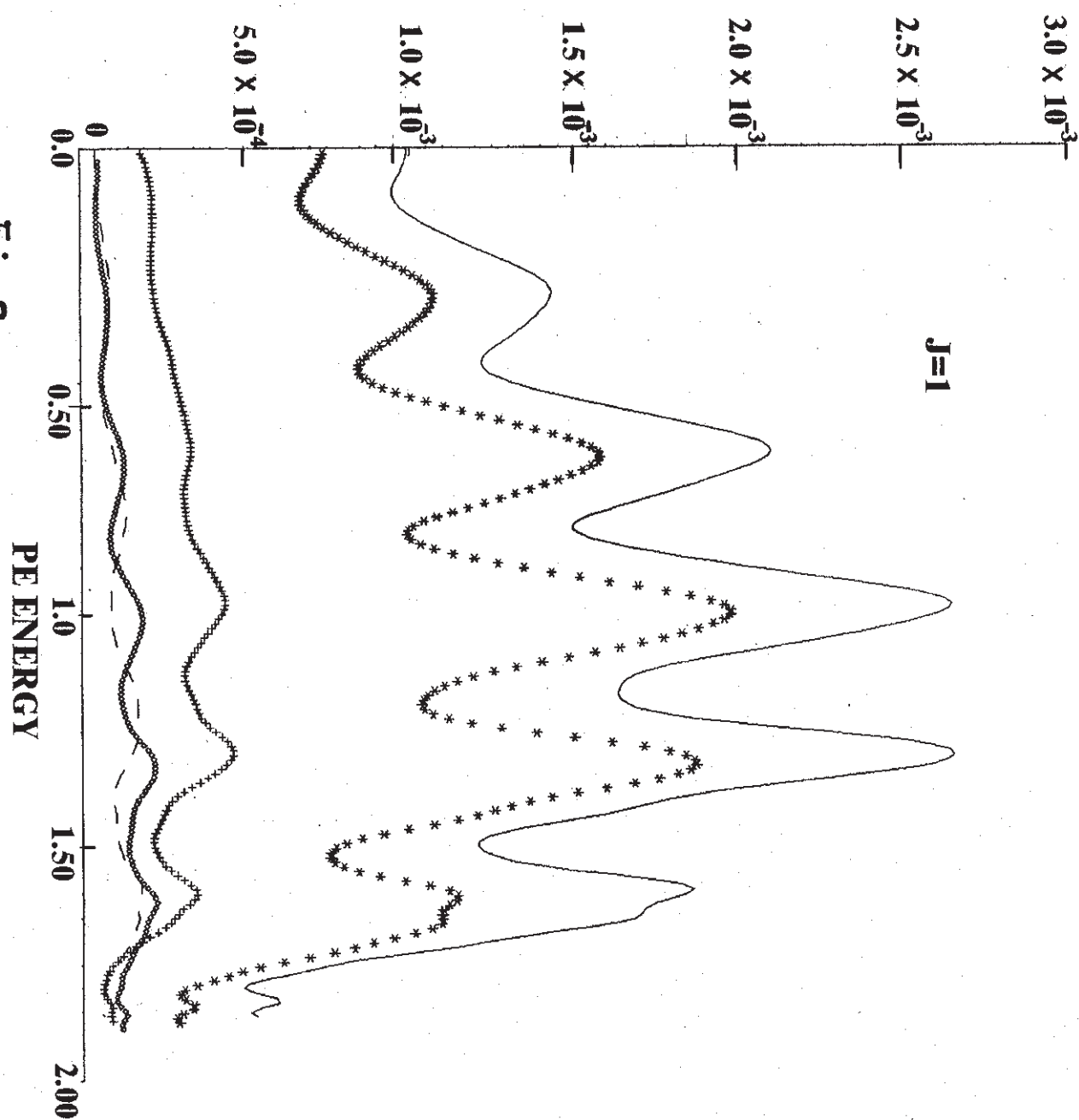


Fig. 3

